

Advances in Conductive Inks across Multiple Applications and Deposition Platforms

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Abstract

Printed Electronics is generally defined as the patterning of electronic materials, in solution form, onto flexible substrates, omitting any use of the photolithography, etching, and plating steps commonly found within the Printed Circuit Board (PCB) industry. The origins of printed electronics go back to the 1960s, and close variants of several original applications and market segments remain active today. Through the 1980s and 1990s Printed Electronic applications based on Membrane Touch Switch and Electroluminescent lighting technologies became common, and the screen printed electronic materials used then have formed the building blocks for many of the current and emerging technologies and applications.

It has been only in recent years that the term Printed Electronics, with the inherent benefits of low cost manufacturing using additive processing, has captured the attention of a much wider audience. One consequence of this attention has been the rush to invest in new materials and patterning processes. While the results so far have generated some as yet unrealized market hype, there are many new and emerging applications that are just entering into production. But instead of requiring radical changes, many of these applications are using screen printed conductive materials that are fundamentally similar to those materials that have been used for over 30 years. We present here a review of both traditional and emerging applications for Printed Electronics, with a focus on the printed functional materials. We also present several recent advances in the capabilities of conductive inks for various deposition methods.

Introduction

Printed Electronics (PE) is not new, but it has been generating a lot of attention and new participants since the mid-2000s. Some of the more traditional applications such as keyboards, appliances, battery testers, electroluminescent lamps, and biosensors date back to the 1970s. Over the past several years there has been an increasing awareness of the potential benefits of PE, especially with the anticipation of electronics printing that can utilize the high volume Roll-to-Roll printing assets that are being made possible through the convergence of the Electronics and Graphics Printing industries.

The commercialization of large-scale printed-electronics devices is contingent on – among many other things – continued progress in the capabilities of the conductive grids, finger lines, shunt lines and bus bars. Due to the different requirements for current handling, registration and topography in different devices, no single deposition method is appropriate. For example, there is an increasing demand for printable conductive tracks in many different application areas such as smart packaging, flexible displays, OLEDs, thin film transistors, thin film photovoltaics, and smart textiles.

For applications where current handling is the key conductor requirement, there are recent advances in low temperature screen printable and extrudable inks that can lay down narrow and high aspect ratio grid lines with excellent line control. With a view to high volume roll-to-roll manufacture, recent developments in inks suitable for gravure and flexographic printing demonstrate they are compatible with novel thermal processing techniques e.g. photonic sintering. Advances in particle and binder technology have led to a dramatic increase in performance of the inks in terms of conductivity, flexibility, line resolution and compatibility with various substrates.

Silver continues to be the primary material of choice for Printed Electronics due to its high conductivity, performance stability, and high volume manufacturability. Most silver inks contain micron sized flakes, but more recently nano-silver compositions have become popular due to the capability of lower temperature sintering (enables increased conductivity) and fine line printing. Nano-silver products are generally more expensive today, however it is expected that production costs will decline when high volume applications requiring nano-silver are commercialized.

For lower cost or less demanding applications, carbon conductors can be printed by screen or flexographic printing. These can be used for conductive tracks in their own right or as overprints on top of silver to protect or prevent silver migration. Specialized carbon compositions have also been developed that can be used as resistors or positive temperature coefficient (PTC) heaters for automotive applications such as external mirror or internal seat heaters.

Dielectrics are an important part of any PE materials system. A dielectric is generally used for its functional properties (capacitor) or as an insulating layer between or on top of conductors. There are many different material types that are used to make a printed dielectric, including thermoplastic and thermosetting plastic polymers. Some dielectrics are thermally cured, while others are cured by UV light.

There are many types of flexible substrates in use with Printed Electronics. Since the device manufacturing process usually starts with the substrate onto which several layers of active and passive material are deposited, the surface needs to be compatible and guarantee processability in subsequent production steps. Polymer films such as the polyester grades (PET, PEN) are most widely used today in printed electronics, but other polymers along with paper and textiles have also been demonstrated. Plastic materials like PET, PEN or PC (polycarbonate) can be tailor-made to adjust physical and surface properties over a wide range so that they can serve as all-round solutions. Other plastics like polyimide (PI), polyethersulfone (PES) or polyetheretherketone (PEEK) with special advantages like increased heat or chemical stability can have higher performance properties and are thus usually considered for higher value applications.

Printed Electronics and Traditional Polymer Thick Film (PTF) Inks:

The term “Printed Electronics” (PE) can have many definitions, but throughout the 2000s it generally refers to the printing of electronic materials onto a flexible substrate. Polymeric Thick Film (PTF) inks have been widely used for the processing of circuit patterns onto plastic and flexible substrates using screen printing technology, and for the most part PTF technology is in use for most of today’s commercial Printed Electronics applications. PTF’s are in the form of a thick film ink or paste, and they are patterned then cured at low temperatures (< 150 °C). PTF inks were first used to manufacture MTS (membrane touch switch) circuits in the 1970s, and they are generally considered a mature and robust technology.

The basic constituents of a PTF conductive ink are the Powder, Resin, and Solvent. The Powder is considered the active element, and ultimately determines the electrical properties of the ink. The Resin provides adhesion to the substrate, cohesion of the conductive powder, and it protects the conductor from external effects. The Solvent controls the viscosity, dissolves the resin, and wets the substrate surface before evaporating during the oven curing process.

The conductive Powder is usually Silver, Carbon, or Gold. Silver is the most widely accepted choice because of its high conductivity and moderate cost, but Carbon and Gold can be used where cost or reliability concerns prevent the use of silver. Critical elements for designing a conductive PTF ink include the particle morphology, the use of surfactant coatings, and the particle packing density to optimize conductivity.

The most common Resin technology is referred to as either Thermoplastic or Thermoset. A thermoplastic resin usually has a lower drying temperature (110-140°C), higher flexibility, and both shrinks during drying and softens on re-heating. A thermoset resin has a higher drying temperature (160-200°C) and reacts during curing to form a rigid structure which cannot be changed with further heating. Critical parameters of polymer resins include Tg of the resin, solubility, molecular weight, and decomposition temperature.

There are many types of solvents used in PTF conductive inks, including glycol ethers, esters, and alcohols. The chosen solvent should be able to effectively dissolve the resin, maintain a balance between varying processing conditions, and consider several environmental concerns including odor and flammability.

The final ink or paste properties are controlled by the % solids, viscosity, Fineness-of-Grind (FOG, to measure powder dispersion), and several functional properties such as resistivity, adhesion, and flexibility. Today there are literally hundreds of commercially available PTF inks in the marketplace, the majority of which have been designed, developed, and modified for patterning by the proven screen print processing. As a result, there are a wide variety of materials available today for Screen Printing, but the choices are limited for alternate patterning technologies such as Ink-Jet, Flexography, and Roto-Gravure.

Traditional PE Applications, and the Materials Used

As stated earlier, there have been many commercial Printed Electronic successes over the past 30+ years, with traditional applications including Membrane Touch Switch, Battery Testers, Biomedical, Electroluminescent lamps, and RFID antenna.

Membrane Touch Switch (MTS) Technology

Perhaps the oldest and most successful of all Printed Electronics applications, MTS uses PTF conductor and dielectric inks to form a mechanical switch that can be built into a label or into a computer keyboard. Silver inks can be screen printed onto two polyester (PET) film layers separated by a spacer layer, and when physically depressed, the two silver traces make a connection. See Figure 1

The silver conductors used to fabricate MTS circuitry typically possess the following properties:

- Resistivity (≤ 15 mohm/sq/mil)
- Good Adhesion to PET Substrate (No Material Removal with Tape)
- Good Abrasion Resistance ($>1H$)
- Good Flexibility

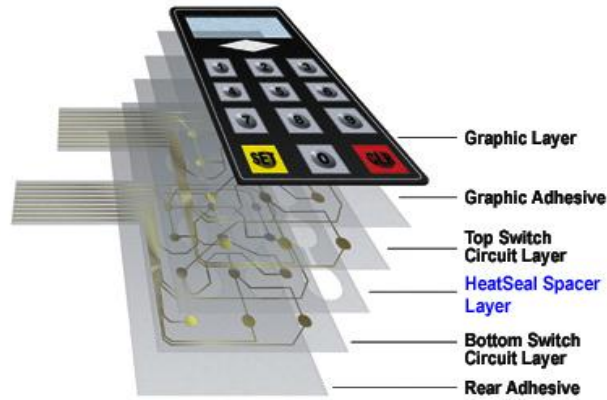


Figure 1 – Membrane Touch Switch (MTS) Circuit

Battery Tester

In the early 1990s, Duracell introduced a Printed Electronic Battery Tester (Figure 2) which was produced by the screen printing of a PTF carbon resistor with PTF silver electrode terminations onto Polyester (PET) substrates. The PTF Resistor was designed to have 70 milliohm/sq/mil Resistivity and to possess excellent Resistance stability ($<5\%$ change) when exposed to high heat and humidity. Prudent choice of resin chemistry and carbon species enabled this technology.

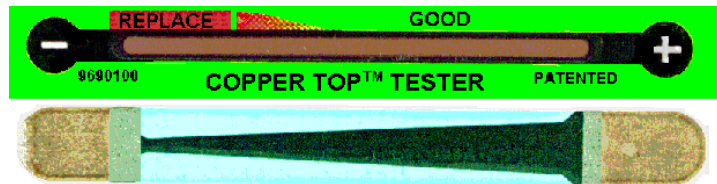


Figure 2 – Duracell AA Battery Tester

Electroluminescent (EL) Technology

During the 1990s, advances in materials and electronics technology plus new demands on lighting technology from the marketplace provided the opportunity for a fundamental shift in the role of electroluminescent (EL) technology. Screen printable multilayer materials systems with compatible conducting, insulating, and luminescent inks helped enable the manufacturing of printed flexible EL lamps for a wide variety of applications, including Point-of-Purchase (POP) signage, nightlights, and backlights for watches and cell phones. The main EL characteristics are:

- Uniform surface illumination of complex shapes
- Thin, flexible and lightweight
- Low power consumption
- Very low heat generation
- Vibration and impact resistant

The EL lamp is essentially a capacitor structure with an inorganic phosphor (zinc sulphide compound) sandwiched between the electrodes (Figure 3). Application of AC voltage across the electrodes generates a changing electric field within the phosphor particles causing them to emit light. For most EL lamps, an inverter (DC-AC converter) is used as a power source.

Light output gradually decays with time, as the luminescent efficiency decreases. The presence of moisture accelerates this decline, as does higher voltages and frequencies. The phosphors common in today's EL inks are microencapsulated to hinder

the penetration of moisture and thus prolong the useful life of the lamps. Likewise the polymer binders in the screen printed inks have been selected to provide a barrier which further protects against moisture-related aging phenomena.

The DuPont™ Luxprint® materials system provides compatible multilayer inks needed to make EL lamps via screen printing onto transparent sputtered ITO (Indium Tin Oxide) polyester substrates.

Today there are some new end use applications under development, but the EL technology remains predominantly a niche technology that continues to be satisfied by the long term availability of screen printed ink systems. Other deposition techniques are suitable for EL materials, but the experience and availability of existing screen print inks suggest it is unlikely the merchant ink suppliers will invest in the development of new materials systems for alternate printing processes.

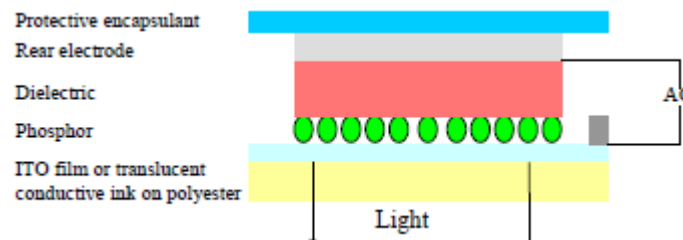


Figure 3 – Electroluminescent Lamp

Biosensors

The screen printing of polymer thick film (PTF) materials is a widely used process for large-scale manufacture of biosensors in medical applications. Blood Glucose sensors are commonly produced by screen printing silver, carbon, and silver/silver chloride PTF compositions onto Polycarbonate (PC) and other substrate materials. The carbon electrode compositions are typically designed for each application and choice of resin, graphite and/or conductive carbon dictates individual performance. Silver/silver chloride compositions are defined by their silver/silver chloride ratios. High silver/silver chloride (65/35 or higher) is best for general glucose sensor applications while low ratios are best suited for Iontophoretic applications due to the specific electrochemical requirements of those cells.

Another Bio application using Printed Electronics is Iontophoretic drug delivery. As shown in Figure 4, Iontophoresis is a non-invasive technique where a small electric current is used to deliver drugs through the skin. Advantages include controlled and continuous delivery of low dosage of medication delivered directly to treatment area, relatively pain free, with better patient compliance.

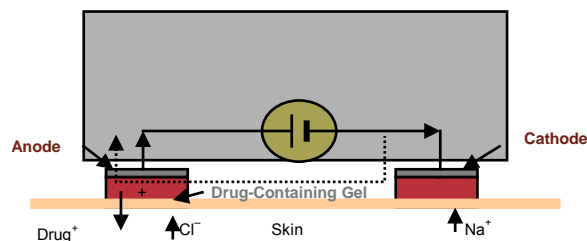


Figure 4 – Iontophoretic Circuit – Zn anode, Ag/AgCl cathode

RFID and Smart Card Antenna

RFID Systems are typically comprised of a primary antenna, a transceiver, and a transponder including a passive antenna. When a passive transponder is passed through an electromagnetic field produced by the primary antenna, its integrated circuit is activated and the information it contains may be read by the transceiver. A critical item of all RFID transponders is the passive antenna technology which must meet three fundamental criteria: it must provide enhanced electronic performance (impedance), permit easy assembly of the IC chip, and allow high volume / low cost production.

A lot has been predicted about how the future of Printed Electronics will include the printing of transistors to replace the RFID chip and chip assembly. If/when this occurs cheaply enough, the addressable opportunity is huge. However and for now, the PE portion is limited to the antenna and in some cases the chip containing strap. Even then, the silver cost of the printed antenna has permitted other technologies such as etched Copper and Aluminum foil to satisfy the low cost requirements. See Figure 5.

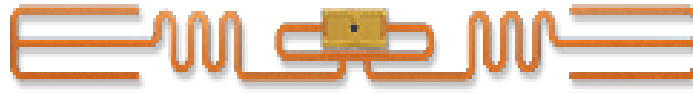


Figure 5 – Etched Copper Antenna – Alien Technologies

Recent advances in Silver conductor technology, plus other cost and environmental concerns, have brought back additive screen printed antenna in some applications. In many cases the new highly conductive silver conductors such as DuPont™ 5064H silver conductor can offer a cost compromise by providing adequate antenna performance with a relatively thin silver print thickness.

Printed Circuit Board (PCB)

Printed Electronic silver and other conductor materials have been used in the construction of PCBs since the 1990s. The most common applications are to provide EMI/RF Shielding, to fabricate low-voltage circuitry, to create a temporary and removable silver “plating link,” and to plug vias with a thermally and electrically conductive material that is plateable. In almost all cases, the patterning is done via screen or stencil printing of a silver, or a silver coated copper conductor. New PTF materials development is ongoing for use by the PCB fabricators, but one general limitation is the limited screen/stencil printing infrastructure and expertise within the board shops.

Emerging PE Applications, and the Materials Used

Many of the Printed Electronic devices described below are nearing or entering commercialization during 2012. As with the traditional PE applications, screen printing is the dominant patterning technology due to decades of experience and the hundreds of commercially available materials. However these newly commercial applications have either required the development of new customized materials, or they have simply replaced alternate wiring with printed conductors within an existing electronic application.

Thin Film Photovoltaic (TFPV)

Thin-Film PV solar cells are becoming more prevalent in the marketplace. The drivers for the growing adoption of Thin-Film PV cells include lower cost structure vs. conventional silicon cells, flexibility of the cells and the ease/cost of manufacturing. Thin-Film cells are usually segmented based upon the semi-conductor or absorber used. This would then include CIGS, a-Si, CdTe, and Organic (Dye Conversion) as the different categories of Thin-Film PV cells. All but CdTe cells can use a front side silver grid as part of the cell construction, and the silver conductors resemble other commercial Polymer Thick Film materials.

Heaters

Although used broadly as a heating element in automotive truck mirrors for years, recent advances in the design and construction of devices containing silver and Positive Temperature Coefficient (PTC) carbon have led to expanded uses of PTF Heater technology. Recent introductions of this technology are being adopted for automotive seat heaters and hypothermia prevention vests where Printed Electronics is replacing resistive wire. Benefits to the end users include safety and reliability, as the PTC carbon is designed to act as a Self Limiting technology that eliminates temperature sensors and controllers while minimizing catastrophic failures. Advanced high conductivity silver helps to lower the overall cost in large area devices.

In-Mold Electronics

The advancement of capacitive touch sensors in devices such as smart phones and tablet PCs is leading towards a new group of PE applications that include in-molded plastics. By nature, capacitive switches are more reliable than mechanical switches as there are no moving parts to wear out or fail. And the ability to print the controls onto a flat surface, then mold into the 3D interior portions of appliances and automotive electronics helps reduce the total space and weight of the final device. Materials required for in-mold products typically consist of Polycarbonate substrates and special PTF conductors that are designed for use on flexible substrates. For example, the silver conductors must maintain good adhesion and low resistivity after the substrate has been creased.

Textiles

Another application that is gaining attention is textiles, or smart clothing. These can be based upon materials that sense and react to environmental conditions or stimuli. Current applications seem focused on printing flexible conductors onto fabrics for use as heaters or other electronic applications. Here the PE conductors must be machine washable, and combine functionality with comfort and aesthetics.

Patterning Techniques – Advanced Screen Printing

Materials must be carefully chosen since process conditions and the interactions with other layers will have a large influence on the performance of the device. These other layers, particularly the dielectric and encapsulant materials, become increasingly important for the overall device performance. There are many approaches - organic or inorganic, solution based or evaporated – and it is very likely that several material and deposition approaches will be used in parallel.

Screen Printing remains the dominant patterning technique used for Printed Electronics, and this is due to the experience and asset base of the established fabricators, plus the availability of hundreds of commercially available inks and pastes that were originally formulated specifically for screen printing. Screen printing is a highly versatile process capable of printing fine lines (60-100 μm) at $\sim 10\ \mu\text{m}$ thicknesses. Advances in screen technology and improvements in processes such as double printing will make lines $\sim 40\ \mu\text{m}$ wide with thicknesses up to $20\ \mu\text{m}$ obtainable. To obtain higher aspect ratios than this, off-contact techniques such as extrusion-based technologies become necessary.

Screen printable PTF compositions typically contain 1-10 micron sized conductive particles, organic resins, solvents and rheology modifiers. The typical solids loading of screen print inks is 50-90% by weight and the dried thicknesses range from 8-15 microns per print. Resolution capabilities are typically 200 micron lines in a high-volume environment and special processing enabling resolution down to 75- 100 microns. The solvents used in screen print inks are fairly slow drying (Boiling Points $>190\text{C}$) and so these inks must be dried at $>100\text{C}$, and preferably $>120\text{C}$.

Patterning Techniques – Roll-to-Roll Printing

A wider range of large area deposition and patterning techniques can now be used for printed electronics, and some of these are being driven by the ongoing convergence of the electronics and packaging graphics industries. The graphic arts industry employs various printing techniques that enable reel-to-reel processing or high speed sheet-to-sheet processing that is considered a requirement for obtaining the lowest possible manufacturing costs.

Rotary screen printing, flexography, gravure and ink-jet printing are all compatible with roll-to-roll, high throughput printing of conductive structures. Many of the challenges are identical to those for screen printable pastes – e.g. low resistivity, fine-line printing, and adhesion – though the methods for achieving these goals may be different. In addition, there are new challenges associated with rapid manufacturing, namely the need for very fast drying or curing of the conductive inks. Photonic curing is one possible means of achieving excellent conductivity in a matter of seconds. Experiments have shown that as well as being very rapid, some improvements in conductivity can be made versus thermal curing.

Flexography is a common print method for packaging graphics. The inks are lower solids than screen print inks; therefore the deposited thickness per pass is also reduced. The solvents used in these inks are also much faster drying than those employed in screen print inks and these inks may be processed at temperatures $<100\text{C}$. Typical thickness for a Flexo deposit is 1-3 microns, while resolution is generally <50 microns. The potential throughput for Flexo inks is much higher than that of screen printed inks – up to 1,000 meters/minute – but the extended drying requirements for electronic materials may prevent the ability to achieve the full print speed potential.

Gravure is also a common print method for packaging graphics. Gravure printing has several advantages for the field of printed electronics, as well as limitations. Gravure allows fine line resolution <50 microns while also permitting a higher ink transfer volume – which is key to conductivity. It is also a high-speed printing process, which makes it ideal for high volume applications. However one negative perception is that gravure being only suitable for high volumes is a key limitation.

Inkjet inks typically are of the solids level of screen print inks, but much lower viscosity. Additionally, because the inks must pass through a rather narrow opening, the particle size of the conductive fillers is smaller than those of screen print inks. Here, the particles must be less than 1 micron, and high aspect ratio lines (50 micron wide and 25 microns thick) may be achieved with these inks. Many of the available inks use silver nano particles, between 0.01 - 0.1 micron.

Advances in Conductors for High Current Devices

For applications where large currents must be carried (e.g. photovoltaic devices, OLEDs, heaters) achieving low resistivity at low temperature is of paramount importance when considering the merits or otherwise of a printed conductive structure. Techniques such as screen printing that can print fine features with high aspect ratio are most suited to such applications. Improving the as-printed resistance can be achieved by: 1) decreased resistivity of the material, 2) improvements in the printability (either printed thickness or uniformity) of the material and 3) advances in thermal processing or alternative curing techniques. All of these are vital to advance the performance of the relevant device but too much emphasis on printability or processing without improving the resistivity of the material can lead to an over consumption of material and associated higher costs of ownership. Hence, current work in this area is focused on improving resistivity, which necessarily means learning better control of the as-printed microstructure.

Historical developments in the properties of materials for thin-film PV devices are shown in Figure 6 showing the continual progress in as-printed performance. The new experimental products offer much improved intrinsic resistivity.

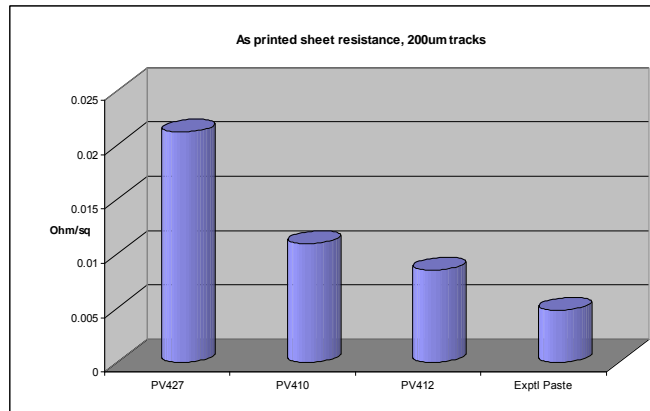


Figure 6. Historical developments in products designed for thin-film PV applications

While conductivity is the key property of these materials, without a combination of properties that includes adhesion (to TCOs and PET) and printability (which considers fine line performance, achievable print speed, smoothness of print and operator friendliness), applicability to real world needs is limited. Future work will combine the best properties of each of these developments and seek to push the performance while decreasing the temperature needed for curing.

Ongoing developments in printed conductors

Developments in printed conductors must continue in order to maximize the performance of printed electronic devices. DuPont has a clear road map for product development which seeks to meet the needs of the market. Figure 7 outlines some of these development paths. It should be noted that while current development is focused on silver, the same paths apply to non-precious metal formulations, with the understanding that these low-cost solutions will be essential for realizing certain applications.

RFID	Smart Packaging	Thin-film PV	OLEDs	Flexible displays
Potential applications				
130-180°C ~20mins		100-130°C ~5mins	<100°C <1min	
Thermal processing requirements				
~100µm tracks ~30 (0.5) m/min		~50µm ~50 (2) m/min	~25µm >100 (10) m/min	
Roll-to-Roll ink flexography (ink-jet) performance				
~100µm 10:1 (width:height)		~70µm 4:1	~50µm 1:1	
Printed tracks for high current applications				
>10µΩ cm >4mΩ/□ @25µm		5-10µΩ cm 2-4 mΩ/□ @25µm	<5µΩ cm <2mΩ/□ @25µm	
Resistivity of printed tracks				
2009		2014		

Figure 7. An outline of some future development paths for printed conductive materials

Summary

Printed Electronics is not new, but activity and market hype over the past several years has led to significant attention and global investments into new materials and patterning technologies that have been intended to enable new high volume “Killer” applications. This is an exciting time for Printed Electronics, and expectations are for continued advances in materials, patterning, and processing technologies. While those types of new materials and products may still emerge successfully within this decade, in many ways it is simply the variants of older and more traditional screen printed Polymer Thick Film materials that are now reaching volume production and thus providing growth opportunities for OEMs, fabricators, and material suppliers.